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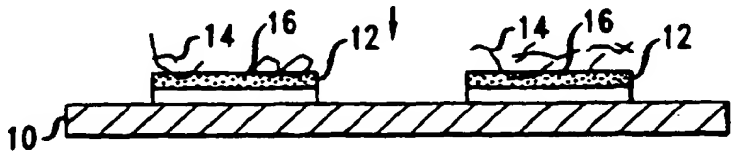
(54) Method for fabrication of patterned carbon nanotube films

(57) A method for fabricating adherent, patterned carbon nanotube films is provided. According to the invention, a substrate is patterned with a carbide-forming material, a carbon-dissolving material, or a low melting point metal. Carbon nanotubes are then deposited onto the patterned substrate, but have relatively poor adhesion to either the substrate material or the patterned material. The substrate is then annealed, typically in vacuum, at a temperature dependent on the particular patterning material, e.g., a temperature at which carbide formation occurs, at which carbon dissolution occurs, or at which the low melting point metal melts. The annealing thereby provides an adherent nanotube film over the patterned areas, while the nanotubes deposited onto the non-patterned areas are easily removed, e.g., by blowing, rubbing, brushing and/or ultrasonication in a solvent such as methanol.

FIG. 1D



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The invention relates to devices comprising carbon nanotube films.

Discussion of the Related Art

[0002] Carbon nanotubes have interesting electronic properties and offer potential for use in electronic devices and in interconnect applications. Carbon nanotubes also feature high aspect ratios (> 1000) and atomically sharp tips which make them ideal candidates for electron field emitters. To realize these potential applications, there is a need to process nanotubes into useful forms such as thin films, and, advantageously, patterned thin films.

[0003] Carbon nanotubes are currently being produced by a variety of different techniques such as arc-discharge, laser ablation and chemical vapor deposition (CVD). (See S. Iijima, Nature, Vol. 354, p. 56 (1991); T.W. Ebbesen and P.M. Ajayan, Nature, Vol. 358, p. 220 (1992); and B.I. Yakobson and R.E. Smalley, American Scientists, Vol. 85, p. 324 (1997). The as-deposited material, however, is usually in the form of loose powders, porous mats, or films with poor adhesion. These forms of nanotubes do not lend themselves to convenient preparation of robust adherent nanotube thin film structures. The difficulty in preparing an adherent film of nanotubes is believed to be due to the perfect structure associated with carbon nanotubes, which contain essentially no dangling bonds and few defect sites. As a result, nanotube films tend to exhibit poor adhesion, even to the point of being easily removed by contact or by air flow (e.g., an air duster).

[0004] Patterned nanotube films have been reported by Fan et al., Science, Vol. 283, p. 512 (1999), and Xu et al., Appl. Phys. Lett., Vol. 74, p. 2549 (1999). These references describe use of direct deposition techniques such as CVD, in which substrates are selectively patterned with catalyst metals and then nanotubes are grown in the patterned areas. These techniques, however, produce films with poor adhesion. The techniques also expose the substrates to a reactive and high-temperature deposition environment, which is both inconvenient and harmful to actual device structures. In addition, the techniques are limited to the patterned growth of multi-wall carbon nanotubes (MWNTs), because CVD typically produce MWNTs on catalytic substrates.

[0005] Thus, there is a desire to develop more convenient and versatile methods for patterning carbon nanotube films with adequate adhesion, to allow formation of more useful and robust device structures.

SUMMARY OF THE INVENTION

[0006] The invention provides a method for fabricating adherent, patterned carbon nanotube films. (Adherent indicates that the adhesion strength of the film exceeds scale 2A or 2B according to ASTM tape testing method D3359-97.) According to the invention, a substrate is patterned with a carbide-forming material, a carbon-dissolving material, or a low melting point metal (i.e., about 700°C or less). Carbon nanotubes are then deposited onto the patterned substrate, e.g., by spraying or suspension casting. The nanotubes have relatively poor adhesion to either the substrate material or the patterned material at this stage. The substrate is then annealed, typically in vacuum, at a temperature dependent on the particular patterning material, e.g., a temperature at which carbide formation occurs, at which carbon dissolution occurs, or at which the low melting point metal melts. The annealing thereby provides an adherent nanotube film over the patterned areas, while the nanotubes deposited onto the non-patterned areas are easily removed, e.g., by blowing, rubbing, brushing, or ultrasonication in a solvent such as methanol. This process provides an adherent nanotube film in a desired pattern. The patterned films are useful for a variety of devices, including vacuum microelectronic devices such as flat panel displays, as well as other structures, e.g., nanotube interconnects.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007]

Figs. 1A-1D illustrate the process of the invention.
Fig. 2 is an optical micrograph of a patterned nanotube film fabricated according to the invention.
Figs. 3A and 3B reflect Raman spectroscopy data indicating the patterned nature of nanotube films fabricated according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The invention provides a process for fabricating patterned, adherent carbon nanotube films. One embodiment of the process is shown in Figs. 1A-1D. Related discussion of adherent nanotube films can be found in U.S. patent application serial no. 09/296,572 (our reference Bower 1-1-37), the disclosure of which is hereby incorporated by reference.

[0009] A flat substrate 10 is first provided. The substrate 10 should be substantially non-reactive with carbon, e.g., not carbide-forming or carbon-dissolving, and should also have a relatively high melting point, typically at least 1000°C. Examples include SiO_2 (including Si wafers having an oxidized surface layer), indium tin oxide (ITO), Al_2O_3, Cu, and Pt.

[0010] As reflected in Fig. 1A, a material 12 is deposited onto the substrate 10 in a pattern desired for

the nanotube film. The patterning material 12 is selected from (a) carbon-dissolving materials, (b) carbide-forming materials, and (c) low melting point (about 700°C or less) metals. Carbon-dissolving materials are known in the art, as reflected, for example in T.B. Massalski, Binary Alloy Phase Diagrams, Vol. I, ASM International, and include elements such as Ni, Fe, Co, and Mn. Carbide-forming elements are similarly known in the art, as reflected in Massalski, supra, and include elements such as Si, Mo, Ti, Ta, W, Nb, Zr, V, Cr, and Hf. Typical low melting point metals include Al, Sn, Cd, Zn, and Bi. The thickness of the patterning material 12 is typically 10 to 100 nm. The patterning material is deposited by any suitable technique, e.g., sputtering, evaporation, or chemical vapor deposition. Conventional lithographic processes are generally used to provide the desired pattern.

[0011] Carbon nanotubes 14 are then deposited onto the patterned substrate 10, as reflected in Fig. 1B. (Only a few nanotubes are shown, for representative purposes, in the drawing - in practice, nanotube coverage would be much more dense.) The nanotubes are typically deposited by suspension casting or spray coating. Suspension casting is generally performed by placing the substrate into a nanotube suspension made up of nanotubes and a solvent such as methanol, and allowing the solvent to evaporate. Spray coating is performed by spraying such a suspension onto the substrate (which is typically heated) using an air gun, and allowing the solvent to evaporate. Both methods tend to provide relatively uniform thin films of randomly oriented nanotubes.

[0012] As reflected in Fig. 1C, the substrate 10 is then annealed, generally in vacuum (10^{-6} torr or less). The temperature of the anneal is selected based on the patterning material 12. Specifically, the temperature is chosen to promote carbon dissolution, carbide formation, or melting of the patterning material 12. The anneal is generally performed 30 minutes to 24 hours, depending on the particular patterning material. By inducing carbon dissolution, carbide formation or melting at the areas where the nanotubes 14 contact the patterning material 12, an area 16 of enhanced adherence between the nanotubes 14 and patterning material 12 is created. Specifically, for carbide-forming material, a carbide is formed by reaction of the material and at least a portion of the nanotubes. For carbon-dissolving material, a metal-carbon solid solution is formed by reaction of the material and at least a portion of the nanotubes. And for low melting point metals, at least a portion of the nanotubes become physically embedded in a molten metal layer and then held in place upon cooling.

[0013] As reflected in Fig. 1D, the nanotubes deposited directly on the substrate 10 material are removed after annealing. Because the nanotubes have relatively poor adherence to the substrate 10 material, removal is relatively easy. Removal is capable of being performed by blowing, rubbing, or brushing the surface of the substrate 10, or by ultrasonication in a solvent such as methanol. It is possible to combine these techniques. Typically, the substrate is ultrasonicated without blowing, rubbing, or brushing. Ultrasonication, when performed without any other removal technique, is generally performed for 0.5 to 24 hours.

[0014] The thickness of the resultant adherent, patterned nanotube film is generally 100 to 1000 nm. The adhesion strength of the resultant patterned nanotube films is sufficient to exceed the 2A or 2B scale in the ASTM tape test D3359-97.

[0015] The patterned nanotube films are useful in a variety of applications, including vacuum microelectronic devices such as flat panel displays, as well as novel applications such as interconnects in silicon-based devices.

[0016] The invention will be further clarified by the following examples, which are intended to be exemplary.

Example 1

[0017] A silicon substrate with an oxidized surface was provided. Al pads having an area of 100 × 70 μm and a thickness of 50 nm were patterned onto the substrate surface by thermal evaporation, using a shadow mask. Single wall carbon nanotubes were obtained. The nanotubes had been fabricated by laser ablation with bundle diameters of 10 to 30 nm and lengths of 2 to 10 μm, and were then purified using an ultrasonically assisted filtration technique (see, e.g., K.B. Shelimov et al., "Purification of Single Wall Nanotubes by Ultrasonically Assisted Filtration," Chem. Phys. Lett., Vol. 282, p. 429 (1998)). The nanotubes were deposited onto the patterned substrate by spraying. The substrate was then vacuum annealed at 700°C for 30 minutes (the melting point of Al is about 660°C), and ultrasonicated in methanol for two hours. The resulting patterned nanotube film is shown in Fig. 2, with coated pads 20, and uncoated substrate surface 22.

Example 2

[0018] A silicon substrate with an oxidized surface was provided. Fe pads having an area of 70 × 70 μm and a thickness of 20 nm were patterned onto the substrate surface by sputtering, using a shadow mask. Single wall carbon nanotubes were obtained as in Example 1. The nanotubes were deposited onto the patterned substrate by spraying. The substrate was then vacuum annealed at 800°C for 30 minutes, and ultrasonicated in methanol for 2 hours. A portion of the resulting structure - coated Fe pad 30 and uncoated substrate surface 32 - is shown in Fig. 3A.

[0019] To confirm that the nanotubes remained intact after the annealing and ultrasonication, Raman spectroscopy was performed. The graphitic carbon-carbon vibration mode at about 1580 cm^{-1} is indicative of

the presence of the nanotube structure. As shown by the Raman spectroscopy results in Fig. 3B, the spectra taken over the Fe pad show nanotubes, while the spectra off the pad indicates the absence of nanotubes.

[0020] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein.

Claims

1. A process for fabricating a patterned, adherent carbon nanotube film, comprising the steps of:

   providing a substrate;
   providing a patterned material on the substrate, the material being selected from the group consisting of carbon-dissolving materials, carbide-forming materials, and low melting point metals;
   depositing carbon nanotubes onto the substrate;
   annealing the substrate to promote adherence of the nanotubes to the patterned material; and
   removing at least a portion of the nanotubes located on the non-patterned area of the substrate.

2. The process of claim 1, wherein the substrate material is selected from the group consisting of SiO_2, indium tin oxide, Al_2O_3, Cu, and Pt.

3. The process of claim 1, wherein the removing step is performed by at least one technique selected from the group consisting of blowing, brushing, rubbing, and ultrasonicating.

4. The process of claim 1, wherein the carbon-dissolving materials are selected from the group consisting of Ni, Fe, Co, and Mn, wherein the carbide-forming elements are selected from the group consisting of Si, Mo, Ti, Ta, W, Nb, Zr, V, Cr, and Hf, and wherein the low melting point metals are selected from the group consisting of Al, Sn, Cd, Zn, and Bi.

5. The process of claim 1, wherein the annealing is performed at a temperature sufficient to attain an effect selected from the group consisting of reaction of at least portion of the nanotubes with the carbon-dissolving material, reaction of at least a portion of the nanotubes with the carbide-forming material, and melting of at least a portion of the low melting point metals.

6. The process of claim 1, wherein the nanotubes are deposited on the substrate by suspension casting or spraying.

7. A device comprising:

   a substrate;
   a patterned material on the substrate; and
   an adherent carbon nanotube film located on the patterned material.

8. The device of claim 7, wherein the patterned material is selected from the group consisting of carbon-dissolving materials, carbide-forming materials, and low melting point metals.

9. The device of claim 8, wherein the carbon-dissolving materials are selected from the group consisting of Ni, Fe, Co, and Mn, wherein the carbide-forming elements are selected from the group consisting of Si, Mo, Ti, Ta, W, Nb, Zr, V, Cr, and Hf, and wherein the low melting point metals are selected from the group consisting of Al, Sn, Cd, Zn, and Bi.

10. The device of claim 7, wherein the nanotubes are single wall nanotubes.

FIG. 1A

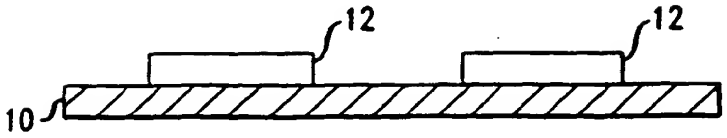


FIG. 1B

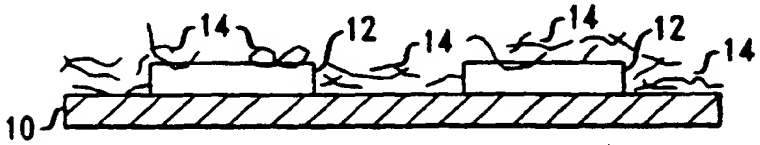


FIG. 1C

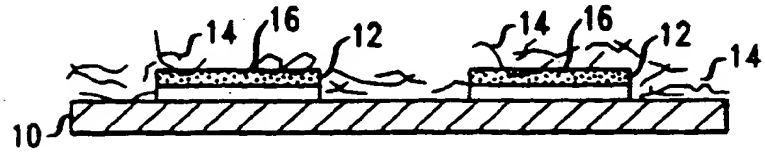


FIG. 1D

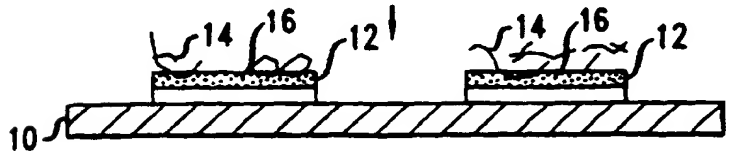


FIG. 2

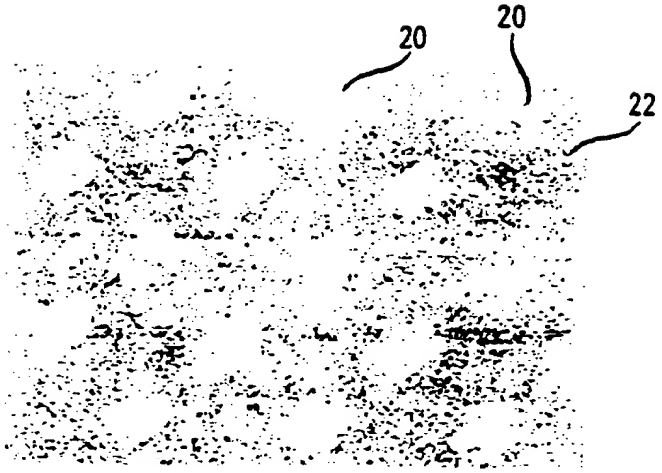


FIG. 3A

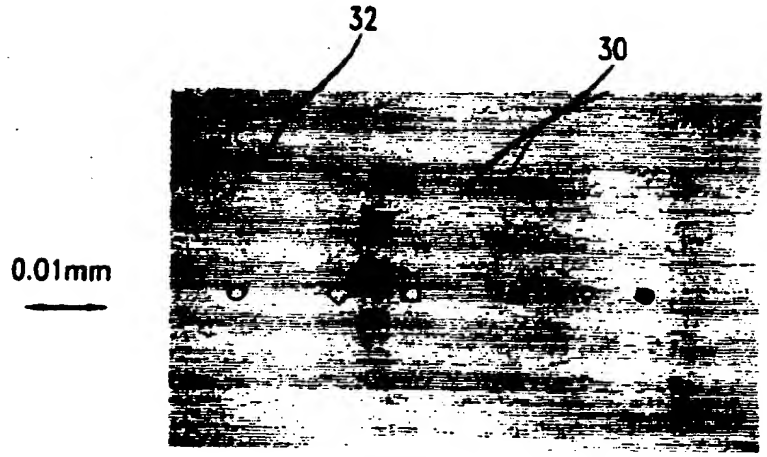
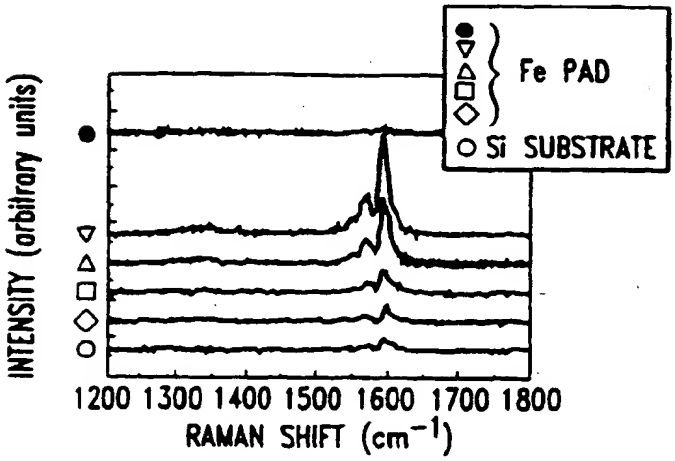


FIG. 3B



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 6690

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	FAN S ET AL: "SELF-ORIENTED REGULAR ARRAYS OF CARBON NANOTUBES AND THEIR FIELD EMISSION PROPERTIES" SCIENCE,AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,,US, vol. 283, 22 January 1999 (1999-01-22), pages 512-514, XP000930011 ISSN: 0036-8075 * page 512; figure 3 *	7-9	H01J9/02 C01B31/02
A		1	
D,A	XU X ET AL: "A METHOD FOR FABRICATING LARGE-AREA, PATTERNED, CARBON NANOTUBE FIELD EMITTERS" APPLIED PHYSICS LETTERS,US,AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 74, no. 17, 26 April 1999 (1999-04-26), pages 2549-2551, XP000829942 ISSN: 0003-6951 * page 2549 *	1,7	
X	WO 98 11588 A (UNIV CALIFORNIA) 19 March 1998 (1998-03-19) * page 7, line 27 - line 31 * * example 4 *	7	TECHNICAL FIELDS SEARCHED (Int.Cl.7) H01J C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	1 November 2000	Colvin, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 6690

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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01-11-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9811588 A	19-03-1998	AU 4269897 A	02-04-1998

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82